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2012 J. Phys.: Conf. Ser. 338 012004

(http://iopscience.iop.org/1742-6596/338/1/012004)

Journal of Physics: Conference Series **338** (2012) 012004 doi:10.1088/1742-6596/338/1/012004

# Account of non-diagonal coupling between *d* electrons at describing the transition-metal pair potentials

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**Abstract.** In the framework of the Wills-Harrison (WH) model the correction due to the non-diagonal coupling between *d* electrons in different atoms is suggested. Effect of this correction on the WH effective pair interaction is studied for liquid Fe, Co, and Ni. It is found that our approach gives a shift of the WH pair potential to the right-hand side for all metals under consideration (in most degree for Fe and in less degree for Ni). As a rule, such tendency leads to significant changes in calculating thermodynamic properties.

## 1. Introduction

The Wills-Harrison (WH) model [1] is widely used in thermodynamics calculations for liquid transition metals and their alloys [2-5]. However, the small argument expansion of the *d*-state radial function was used to obtain the effective pair potential in Ref. [1]. Only diagonal *d-d* coupling between different atoms arises in the framework of that approximation. At the same time, an influence of the non-diagonal coupling to the transition-metal potential energy can be significant. The difficulty is that the deviation from the diagonal coupling can not be expressed in the exact form.

Here, we introduce the probability that not only the diagonal coupling is possible between *d* electrons centred at the neighbouring atoms, and study how the WH potential corrected by such a way depends on the magnitude of this probability. In fact, this correction gives an additional magnetic contribution to the pair interaction due to the indirect orbital interaction between *d* electrons of different atoms. The WH effective pair potentials are investigated in pure liquid Fe, Co, and Ni near their melting temperatures.

## 2. Theory

Wills and Harrison [1] presented the effective pair potential for transition metals as a sum of two terms. The first one arises due to *d* electrons, while the second is taken from the nearly-free-electron (NFE) theory (with the effective number of valence *s* electrons per atom - $z_s$):

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$$V_{\mathrm{WH}}(r) = V_d(r) + V_{\mathrm{NFE}}(r), \tag{1}$$

Following to Refs. [4, 5], we use the Bretonnet-Silbert (BS) local model pseudopotential [6] to calculate the contribution $V_{\mathrm{NFE}}(r)$. The exchange-correlation function is taken in the Vashishta-Singwi form [7].

The *d*-electron-dependent part of the WH potential consists of two terms – the contribution $V_b(r)$ due to the *d*-band width, and the contribution $V_c(r)$ due to the shift of the *d*-band heavy centre with respect to the *d* level of the single atom (hereafter, in the atomic units (a.u.)):

$$V_d(r) = V_b(r) + V_c(r), \tag{2}$$

$$V_b(r) = -K_b\left(\frac{10 - z_d}{10}\right)\left(\frac{12}{a}\right)^{1/2}\frac{z_d r_d^3}{r^5}, \tag{3}$$

$$V_c(r) = K_c\frac{z_d r_d^6}{r^8}, \tag{4}$$

where $z_d$ is the effective number of valence *d* electrons per atom, $r_d$ is the *d*-state radius, $a$ is the coordination number (taken for each Fe, Co, and Ni equal to 12), $K_b$ and $K_c$ are some coefficients.

Wills and Harrison used the small argument expansion of the *d*-state radial function, which gives only diagonal coupling between *d*-electron states of different atoms with respect to the magnet quantum number, *m* ( i.e. the coupling between *d* electrons with the same *m* only is possible). In this case, for the orbital quantum number $l = 2$,

$$K_b = \left(\sum_{m=-2}^{2}\frac{y_m^2}{5}\right)^{\frac{1}{2}}, \tag{5}$$

$$K_c = -2\sum_{m=-2}^{2}\frac{y_m x_m}{5}, \tag{6}$$

where $y_m$ and $x_m$ are combinatoric coefficients:

$$y_m = -\frac{(-1)^m 180}{\pi(2+m)!(2-m)!}, \tag{7}$$

$$x_m = -\frac{1}{8}\left(1 + \frac{4m^2 - 1}{9}\right)y_m. \tag{8}$$

From Eqs. (5) – (8)

$$K_b = \frac{28.06}{\pi}, \tag{9}$$

$$K_c = \frac{225}{\pi^2}\,. \tag{10}$$

In the case when only diagonal coupling is possible, there are only 5 equiprobable couplings between two atoms, and the multiplier 1/5 in Eqs. (5), (6) corresponds to this case.

On the contrary, when a free change of $m$ is allowed for the $d$-state coupling, there are 25 equiprobable couplings between two atoms and instead of Eqs. (5), (6) we have the following equations (denote $y_m = y_{|m|}$ and $x_m = x_{|m|}$):

$$K_b = \left( \frac{y_0^2}{25} + \frac{4y_1^2}{25} + \frac{4y_2^2}{25} + \frac{4y_0y_1}{25} + \frac{4y_0y_2}{25} + \frac{8y_1y_2}{25} \right)^{\frac{1}{2}}, \tag{11}$$

$$K_c = -2\left( \frac{y_0x_0}{25} + \frac{2y_0x_1}{25} + \frac{2y_0x_2}{25} + \frac{2x_0y_1}{25} + \frac{2x_0y_2}{25} + \frac{4y_1x_1}{25} + \frac{4y_1x_2}{25} + \frac{4y_2x_1}{25} + \frac{4y_2x_2}{25} \right), \tag{12}$$

Let us now denote the probability that not only diagonal coupling is possible as $p$. Then, the probability that only diagonal coupling is possible will be $(1-p)$, and the resulting expressions for $K_b$ and $K_c$ became as follows:

$$K_b = \left[ \frac{1}{5}\left( \left(1 - \frac{4p}{5}\right) y_0^2 + \left(2 - \frac{6p}{5}\right)(y_2^2 + y_1^2) + \frac{4p}{5} y_0(y_1 + y_2) + \frac{8p}{5} y_1y_2 \right) \right]^{\frac{1}{2}}, \tag{13}$$

$$K_c = -\frac{2}{5}\left[ \left(1 - \frac{4p}{5}\right) y_0x_0 + \left(2 - \frac{6p}{5}\right)(y_1x_1 + y_2x_2) + \frac{2p}{5}(y_0(x_1 + x_2) + x_0(y_1 + y_2)) + \frac{4p}{5}(y_1x_2 + y_2x_1) \right] \tag{14}$$

At $p = 0$, Eqs. (13) and (14) lead to Eqs. (9) and (10), and at $p = 1$ to Eqs. (11) and (12), respectively.

## 3. Results and Discussion

The effective pair potentials of pure liquid Fe, Co, and Ni near the melting points are considered. Needed values of the mean atomic volume, $\Omega$, for each metal are taken from experiment [8] and are listed in Table 1. The BS parameters, $R_c$ and $A$, and the WH parameter, $r_d$, are taken from Refs. [9] and [1], respectively (Table 1). $z_d$ is defined as $(z - z_s)$, where $z$ is the total number of valence electrons per atom. For all three metals $z_s$ equal to 1.4 following to Ref. [9].

Pair potentials near their first minimums at different $p$ are presented in Figs.1-3. It is found that with increase of the $p$ magnitude the position of the first minimum of the pair potential is being shifted to larger $r$ and its depth becomes smaller in all cases independently on the kind of the metal. Both above tendencies are most sharp for Fe, intermediate for Co, and lowest for Ni.

**Table 1.** Input data for calculations

| | Fe | Co | Ni |
|---|---|---|---|
| $r_d$ (a.u.) | 1.512 | 1.437 | 1.342 |
| $z_d$ | 6.6 | 7.6 | 8.6 |
| $R_c$ (a.u.) | 1.540 | 1.641 | 1.030 |
| $A$ (a.u.) | 0.363 | 0.393 | 0.207 |
| $\Omega$ (a.u.) | 89.29 | 85.85 | 85.24 |

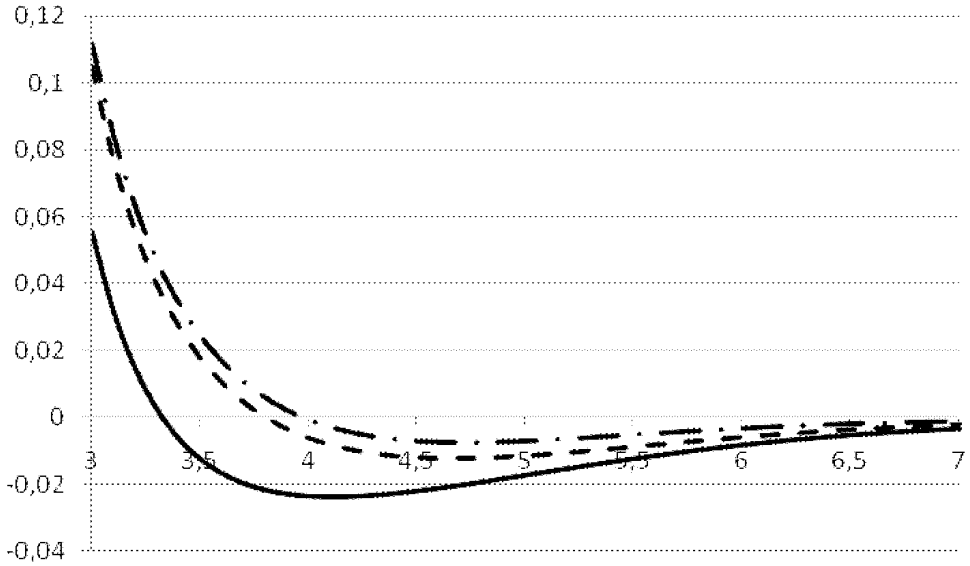


**Figure 1.** $V_{\mathrm{WH}}(r)$ at $p = 0$ (Fe – solid line; Co – dashed line; Ni – dashed-dotted line)

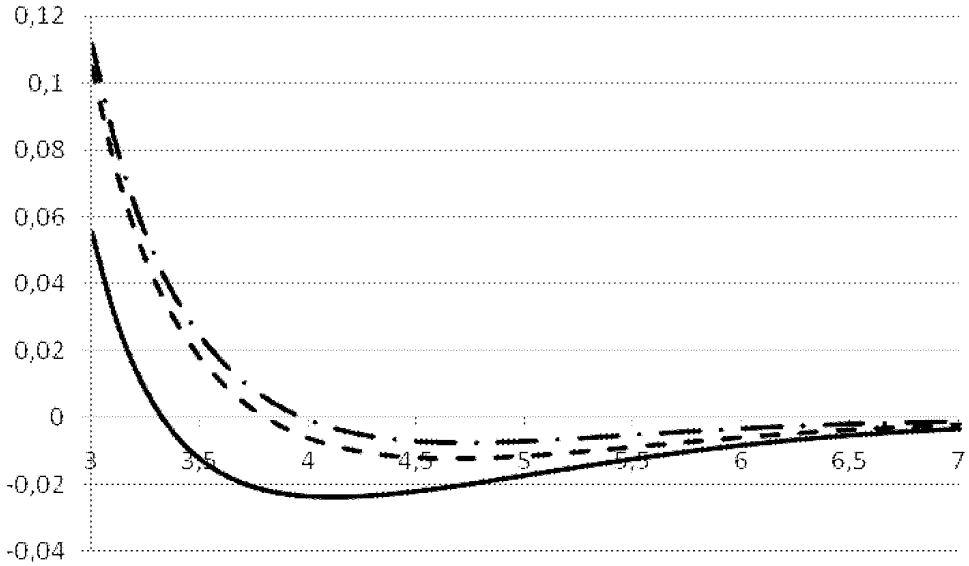


**Figure 2.** $V_{\mathrm{WH}}(r)$ at $p = 0.5$ (Fe – solid line; Co – dashed line; Ni – dashed-dotted line)

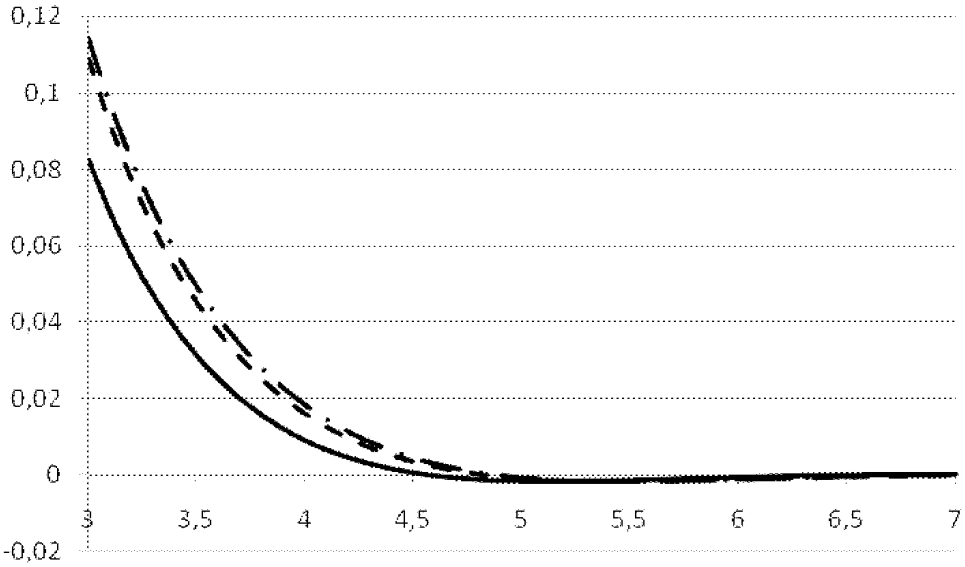


**Figure 3.** $V_{\mathrm{WH}}(r)$ at $p=1$ (Fe – solid line; Co – dashed line; Ni – dashed-dotted line)

## 4. Conclusion

Results obtained show that the suggested correction of the WH model leads to significant changes in the corresponding pair interaction. Since the behaviour of the effective pare potential influences on thermodynamic properties, it is possible to conclude that this correction will give more considerable changes for liquid Fe-Co alloy and less considerable for Co-Ni one in future thermodynamics calculations.

## Acknowledgments

This work is supported by the Ural Branch of the Russian Academy of Sciences, and Russian Ministry of Science and Education (contract 02.740.11.0641).

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